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Girard T Hydrazones of 2-Alkanones, *n*-Alkanals, Alk-2-enals, and Alk-2,4-dienals

There is scanty information in the literature (1) concerning Girard T hydrazones of aliphatic monocarbonyl compounds. Seligman, Edmonds, O'Keeffe, and Lee (2) reported difficulty in preparing well-defined crystalline Girard T hydrazones of the methyl ketones, *n*-alkanals, alk-2-enals, and alk-2,4-dienals. Nevertheless, the gums and semisolids moved in solution on filter paper to give reproducible R_f values.

The Girard T reagent and its water-soluble derivatives have many useful properties. It has been shown to be capable of quantitative recovery of the three classes of *n*-aldehydes from fats and oils (3). In reaction and isolation of aldehydes from labile systems, such as autoxidized fat, the reagent appears to come closest to the separation of the actual free aldehydes present (4, 5). Furthermore, the ease of hydrolysis of its derivatives under mild conditions makes it potentially superior in this respect to 2,4-dinitrophenylhydrazones in gas chromatographic applications (6). As a preliminary step to study of chromatographic systems of separating Girard T hydrazones of aliphatic aldehydes and ketones, crystalline derivatives have been prepared, and the properties of representative compounds are reported in this communication.

Methods. Girard T derivatives of *n*-aldehydes and methyl ketones were prepared as described by Gaddis *et al.* (3, 7, 8). A 20% excess of monocarbonyl compound was added to facilitate purification. The reaction mixture was distilled at reduced pressure until a gummy distilland was obtained. This was treated with a portion of ethanol and the distillation repeated to aid in the removal of water. The gummy and sometimes semisolid residue was taken up in a minimum amount of *tert*-butyl alcohol. If the bulk of the residue was resistant to solution, a little ethanol was added to facilitate the process. The solution was filtered. Girard T reagent is sparingly soluble in *tert*-butyl alcohol. Crystallization was initiated by careful addition of small amounts of petroleum ether followed by cooling. Separated crystals were washed while still wet with petroleum ether, and immediately freed of solvent in a vacuum desiccator. Recrystallization gave constant melting points. Solids were dried in an Abderhalden drying pistol. The ultraviolet spectrophotometric properties, recovery by conversion to 2,4-dinitrophenylhydrazones, and nitrogen content of the crystalline solids were determined. Spectrophotometric measurements of Girard T hydrazones were made in ethanol and 2,4-dinitrophenylhydrazones in carbon tetrachloride. The Girard T hydrazones were converted to 2,4-dinitrophenylhydrazones as described by Gaddis *et al.* (3). Nitrogen content was measured by micro-Kjeldahl determination using the digestion method of Fish (9).

Results and Discussion. Results are shown in Table 1. The span in wavelength of maximum absorption was much wider in aldehyde classes of Girard T derivatives than with similar 2,4-dinitrophenylhydrazones (10). Molecular extinction coefficients of alkanals and 2-alkanones were lower, and alk-2-enals and alk-2,4-dienals higher than comparable 2,4-dinitrophenylhydrazine derivatives (10). Recoveries as 2,4-dinitrophenylhydrazones and the nitrogen analyses demonstrate that the crystalline solids are authentic Girard T hydrazones. These crystalline solids

TABLE 1
PROPERTIES OF SOME GIRARD T HYDRAZONES

Girard T hydrazones	λ_{max} mμ	Molecular extinction coefficient	M.p., °C (uncorr.)	Recovery as 2,4-DNPH %	Nitrogen analysis		
					Formula	Per cent N_2 Theor.	Found
Alkanals							
C-3	229	13,248	169–70	93.1			
C-6	229	14,516	163–64	97.0	$C_{11}H_{24}N_3OCl$	16.83	16.99
C-10	229	14,008	158–59	95.0			
Alk-2-enals							
C-4	265	29,931	182–83	97.0	$C_9H_{18}N_3OCl$	19.13	18.94
C-10	268	28,790	136–37	103.0			
Alk-2,4-dienals							
C-6	297	45,746	163–64	93.4	$C_{15}H_{28}N_3OCl$	13.93	13.60
C-10	297	47,597	180–81	95.1			
2-Alkanones							
C-3	233	13,362	123–24	101.5			
C-7	233	13,380	113–14	102.5	$C_{12}H_{25}N_3OCl$	15.99	15.25
C-11	233	13,221	129–30	98.4			

are therefore suitable for paper and thin-layer chromatographic studies on the separation of complex mixtures of the four homologous series of monocarbonyl compounds.

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